

Samples have been furnished in this case under Section 2, Sub-section 5, of the Patents and Designs Acts, 1907 to 1928.

PATENT SPECIFICATION.

Application Date : Nov. 4, 1929. No. 33,493 / 29.

344,409

Complete Left : June 23, 1930.

Complete Accepted : March 4, 1931.



PROVISIONAL SPECIFICATION.

Improvements in and relating to the Manufacture of Intermediates and Dyes from Heterocyclic Nitrogen Compounds.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a company incorporated under the laws of Great Britain, HENRY ALFRED PIGGOTT and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British subjects, do hereby declare the nature of this invention to be as follows:—

Our invention relates to new methods of preparing intermediates and dyestuffs.

We have found that diarylformamidines interact with heterocyclic nitrogen compounds containing reactive methyl or reactive external methylene groups, these compounds being in the form of cyclic ammonium salts or the corresponding bases. The products, according to conditions, are either intermediates for dyes or dyes themselves. We treat, for example, 2:3:8-trimethylindolenine methiodide with diphenylformamidine by heating them together alone or in a suitable solvent (e.g. acetic anhydride). We thus obtain, when interaction takes place between one molecular proportion of each compound, a new substance which is a valuable intermediate. When more than one molecular proportion of the trimethylindolenine methiodide reacts, the dyestuff described below is also formed; but satisfactorily to obtain it alone we prefer to treat 1:3:8-trimethyl-2-methyleineindoline, which is the (pseudo-) base corresponding with the above iodide, in a similar way with one half molecular proportion of diphenylformamidine dissolved in acetic anhydride. On subsequently dissolving the product in a mineral acid, e.g. hydrochloric acid, we obtain the dye known as 1:3:8:1':3':8'-hexamethylindocarbocyanine chloride (Journal of the Chemical Society, 1927, 2796).

Our invention is applicable generally to heterocyclic ammonium salts containing reactive methyl groups or to the corresponding pseudo-bases containing re-

active external methylene groups.

By our invention we obtain new and valuable compounds of a hitherto unknown type; further we obtain known dyestuffs by a novel process which exhibits important technical advantages.

Our invention is illustrated, but not limited, by the following examples, in which the parts are by weight.

EXAMPLE 1.

6 parts of 2:3:8-trimethylindolenine methiodide and 4 parts of diphenylformamidine are mixed with 50 parts of acetic anhydride and the mixture is boiled under reflux for 40 minutes. On cooling the new compound separates as a mass of crystals, which are filtered off and washed with acetic anhydride.

EXAMPLE 2.

60 parts of quinaldine ethiodide and 40 parts of diphenylformamidine are intimately mixed together and slowly heated to 180° C. The mixture becomes at first pasty or fluid but later becomes stiffer and more solid. The product is removed from the reaction vessel, pulverised, washed with dilute hydrochloric acid to remove the aniline which is a by-product of the reaction, again washed with water, and dried.

EXAMPLE 3.

85 parts of 1:3:8-trimethyl-2-methyleineindoline and 25 parts of diphenylformamidine (i.e. rather more than the theoretical amount) are dissolved in 300 parts of acetic anhydride and the solution is boiled under reflux for 1 hour. The solvent is then removed by distillation. The residue is boiled with 300 parts of hydrochloric acid (20%). The solution obtained deposits the dyestuff 1:3:8:1':3':8'-hexamethylindocarbocyanine chloride, on cooling. The product is filtered off and dried.

Dated the 4th day of November, 1929.

E. C. G. CLARKE,

Imperial Chemical House, Millbank,
London, S.W.1.

Solicitor for the Applicants.

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COMPLETE SPECIFICATION.

Improvements in and relating to the Manufacture of Intermediates and Dyes from Heterocyclic Nitrogen Compounds.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a company incorporated under the laws of Great Britain, HENRY ALFRED PIGGOTT and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Our invention relates to new methods of preparing intermediates and dyestuffs.

We have found that diarylformamidines interact with heterocyclic nitrogen compounds, containing reactive methyl or reactive external methylene groups, these compounds being in the form of cyclic ammonium salts or the corresponding pseudo-bases. The products according to conditions, are either intermediates for dyes or dyes themselves.

We treat, for example, 2:3:8-trimethylindolenine methiodide with diphenyl formamide by heating them together, alone or in a suitable solvent (e.g. acetic anhydride). We thus obtain, when interaction takes place between one molecular proportion of each compound, a new substance which is a valuable intermediate. When more than one molecular proportion of the trimethylindolenine methiodide reacts, the dyestuff described below is also formed, but satisfactorily to obtain it alone we prefer to treat 1:8:8-trimethyl - 2 - methyleneindoline, which is the (pseudo-) base corresponding with the above iodide, in a similar way with one half molecular proportion of diphenylformamide dissolved in acetic anhydride. On subsequently dissolving the product in a mineral acid, e.g. hydrochloric acid, we obtain the dye known as 1:8:8:1':3':8': - hexamethylindocarbocyanide chloride (Journal of the Chemical Society, 1927, 2796).

Our invention is applicable generally to heterocyclic ammonium salts containing reactive methyl groups or to the corresponding pseudo-bases containing reactive external methylene groups.

By our invention we obtain new and valuable hitherto unknown intermediate compounds; further we obtain known dyestuffs by a novel process which exhibits

important technical advantages.

Corresponding products are obtained when, instead of using 2:3:8-trimethylindolenine methiodide or the pseudo-base, we use other heterocyclic nitrogen compounds containing external reactive methyl or methylene groups, e.g. the metho- or etho-halides of 2- or 4-methylquinoline, 2-methylbenzoxazole or 2-methylbenzthiazole or the corresponding pseudo-bases (when obtainable). We may vary the procedure, sometimes advantageously, by using a salt of the diarylformamidines together with the pseudo-bases; indeed it appears necessary to have acid present when the pseudo-base is used except when an acid-producing solvent such as acetic anhydride is used.

The intermediate compounds formed from equimolecular proportions of the two reacting substances appear to be, when e.g., diphenyl-formamide is used, anilino-vinyl compounds of the heterocyclic salt. When acetic anhydride is used as solvent, the acetyl derivative of this anilino-vinyl compound is obtained. When this acetyl derivative is subjected to an appropriate hydrolytic treatment e.g. by heating with concentrated hydrochloric acid, the acetyl group is removed. On the other hand, when 1:8:8-trimethyl-2-methyleneindoline is simply heated with diphenylformamide hydrochloride the corresponding 8:8-dimethyl-2-anilino-vinylindolenine methochloride is obtained directly.

In effecting our invention with the object of making dyestuffs we do not limit ourselves to one particular mode of procedure. Thus, we may cause two molecular proportions of, e.g., 1:8:8-trimethyl-2-methyleneindoline to interact with one molecular proportion of free diarylformamide in hot-acetic anhydride, or with one molecular proportion of diaryl formamide hydrochloride alone or in acetic anhydride or pyridine or a neutral solvent; or we may simply heat together one molecular proportion of the pseudo-base, one molecular proportion of the corresponding halide, and one molecular proportion of diarylformamide; or we may cause to interact two molecular proportions of the heterocyclic salt with one molecular proportion of diarylformamide in presence of one molecular proportion of such an acid

binding agent as sodium acetate.

The process according to our invention has many advantages over known methods for the manufacture of polymethine dyestuffs. A known method for producing these dyestuffs involves the use of ethyl orthoformate. This reagent is expensive and difficult to prepare and is of limited applicability. By our method, as has been explained, intermediate condensation products are obtained, which can be used for the manufacture of dyestuffs. Further, diarylformamidines are readily accessible, diphenylformamidine for example being obtained simply by heating together aniline and formic acid. The aniline can be recovered.

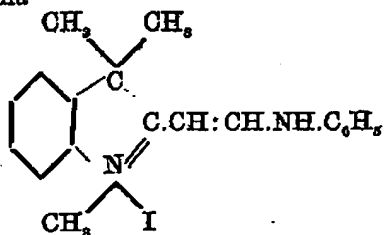
Our invention is illustrated, but not limited, by the following examples, in which the parts are by weight.

EXAMPLE 1.

6 parts of 2:8:8-trimethylindolenine methiodide and 4 parts of diphenylformamidine are mixed with 50 parts of acetic anhydride and the mixture is boiled under reflux for 40 minutes. On cooling the new compound separates as a mass of crystals, which are filtered off and washed with acetic anhydride. This product is the acetyl derivative of the product of Example 2. It has m.p. 260° (decomp.)

EXAMPLE 2.

The product from Example 1 is dissolved in hot concentrated hydrochloric acid. Almost immediately a new crystalline substance begins to separate. Separation being complete, the suspension is cooled and filtered. When the product is recrystallised from water or dilute alcohol it has m.p. 248—244°. To this compound is probably to be attributed the formula



EXAMPLE 3.

30 parts of 2:8:8-trimethylindolenine methiodide and 20 parts of diphenylformamidine are mixed together and heated in an appropriate jacketted vessel at 200° C. The mixture rapidly becomes transformed into a dark red molten mass, which is allowed to cool slowly to 120°. 60 parts of alcohol are added, the crystalline product is filtered off, washed with alcohol and recrystallised from water. This product is identical with that of Example 2. From the alcoholic mother liquors and washings a small proportion

of the dye 1:3:3:1':3':3':-hexamethylindocarbocyanine iodide, formed as a by-product, can be separated.

EXAMPLE 4.

A solution of 58 parts of 2-methylbenzoxazole ethiodide and 40 parts of diphenylformamidine in 250 parts of acetic anhydride is heated to boiling for 20 minutes. On cooling, the new compound, probably acetanilidovinylbenzoxazole ethiodide m.p. 227° (decomp.) separates.

EXAMPLE 5.

A solution of 90 parts of 2-methylbenzothiazole ethiodide and 66 parts of diphenylformamidine in 500 parts of acetic anhydride is heated to boiling for 20 mins. On cooling a crystalline product, m.p. 229°, probably 2- ω -acetanilidovinylbenzothiazole ethiodide separates.

EXAMPLE 6.

60 parts of quinaldine ethiodide and 40 parts of diphenylformamidine are intimately mixed together and slowly heated to 180° C. The mixture becomes at first pasty or fluid but later becomes stiffer and more solid. The product is removed from the reaction vessel, pulverised, washed with dilute hydrochloric acid to remove the aniline which is a by-product of the reaction, again washed with water, and dried.

EXAMPLE 7.

35 parts of 1:3:3-trimethyl-2-methyleneindoline and 25 parts of diphenylformamidine are dissolved in 800 parts of acetic anhydride and the solution is boiled under reflux for 1 hour. The solvent is then removed by distillation. The residue is boiled with 300 parts of hydrochloric acid (20%). The solution obtained deposits the dyestuff 1:3:3:1':3':3'-hexamethylindocarbocyanine chloride, on cooling. The product is filtered off and dried.

EXAMPLE 8.

35 parts of 1:3:3-trimethyl-2-methyleneindoline and 28.5 parts of diphenylformamidine hydrochloride are heated together as described in Example 3 at 145—150° C. for 1 hour. The mixture is then cooled and dissolved in 1100 parts of hot 15% hydrochloric acid. From this solution, on cooling the dyestuff 1:3:3:1':3':3'-hexamethylindocarbocyanine chloride separates in a very pure state.

EXAMPLE 9.

A mixture of 35 parts of 1:3:3-trimethyl-2-methyleneindoline, 28.5 parts of diphenylformamidine hydrochloride and 40 parts of acetic anhydride is heated with stirring in a vessel fitted with a reflux condenser at 145—150° C. for 1 hour. The product is then dissolved in 1100 parts of 15% hydrochloric acid and the dyestuff

is isolated as in the preceding example.

EXAMPLE 10.

A solution of 80 parts of 2-methylbenzothiazole ethiodide, 11 parts of diphenylformamidine and 5 parts of anhydrous sodium acetate in 250 parts of acetic anhydride is heated to boiling for 30 mins. and allowed to cool. The dye that separates is 1:1'-diethylcarbothiocyanine iodide (Mills, Journal of the Chemical Society, 1922, vol. 121, page 462).

EXAMPLE 11.

A mixture of 22.5 parts of quinaldine ethiodide, 8.8 parts of diphenylformamidine, 4.2 parts of sodium acetate and 187.5 parts of acetic anhydride is treated as described in Example 10. There is obtained the dyestuff known as pinacyanol. (Journal of the Chemical Society, 1922, vol. 117, page 1550).

In place of diphenylformamidine, there may be used in any of the above examples, other diarylformamidines, e.g. *pp'*-dichlorodiphenylformamidine, *di-p*-tolylformamidine, etc.

The following samples, together with dyeings on wool and cotton of Sample No. 5 have been furnished in connection with this specification under Section 2 (5) of the Patents Acts.

SAMPLE No. 1.

2- ω -Acetanilidovinyl - 3:3: - dimethylindolenine methiodide. (Product of Example 1).

SAMPLE No. 2.

2- ω -Anilinovinyl - 3:3 - dimethylindolenine methiodide. (Product of Example 2).

SAMPLE No. 3.

2- ω -Acetanilidovinylbenzoxazole ethiodide. (Product of Example 4).

SAMPLE No. 4.

2- ω -Acetanilidovinylbenzthiazole ethiodide. (Product of Example 5.)

SAMPLE No. 5.

1:3:3:1':3':3' - Hexamethylindocarbocyanine chloride. (Product of Example 7), giving blue-red shades on cotton and red on wool.

SAMPLE No. 6.

Product from γ -methylquinoline

methiodide and diphenyl formamidine, i.e. 4- ω -anilinovinylquinoline methiodide, m.p. 255-260° (decomp.).

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of dyestuff intermediates which comprises the interaction of substantially equimolecular proportions of a diarylformamidine and a heterocyclic nitrogen compound which contains a reactive methyl or reactive external methylene group, the heterocyclic nitrogen compound being either a cyclic ammonium salt or the corresponding pseudo-base, in the presence or absence of a solvent, at least one molecular proportion of an acid being present either in the free state or combined with one or both of the ingredients.

2. Process for the manufacture of dyestuffs of the polymethine series which comprises the interaction of substantially one molecular proportion of a diarylformamidine and substantially two molecular proportions of a heterocyclic nitrogen compound which contains a reactive methyl or reactive external methylene group, the heterocyclic nitrogen compound being either a cyclic ammonium salt or the corresponding pseudo-base, in the presence or absence of a solvent, at least one molecular proportion of an acid being present either in the free state or combined with one or both of the ingredients.

3. Process for the manufacture of intermediates or dyestuffs substantially as described in each of the Examples hereinbefore set out.

4. Products obtainable according to the process of any of the preceding claims whenever made by such process or its obvious chemical equivalent.

Dated the 20th day of June, 1930.

E. C. G. CLARKE,
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London, S.W.1,
Solicitor for the Applicants.

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